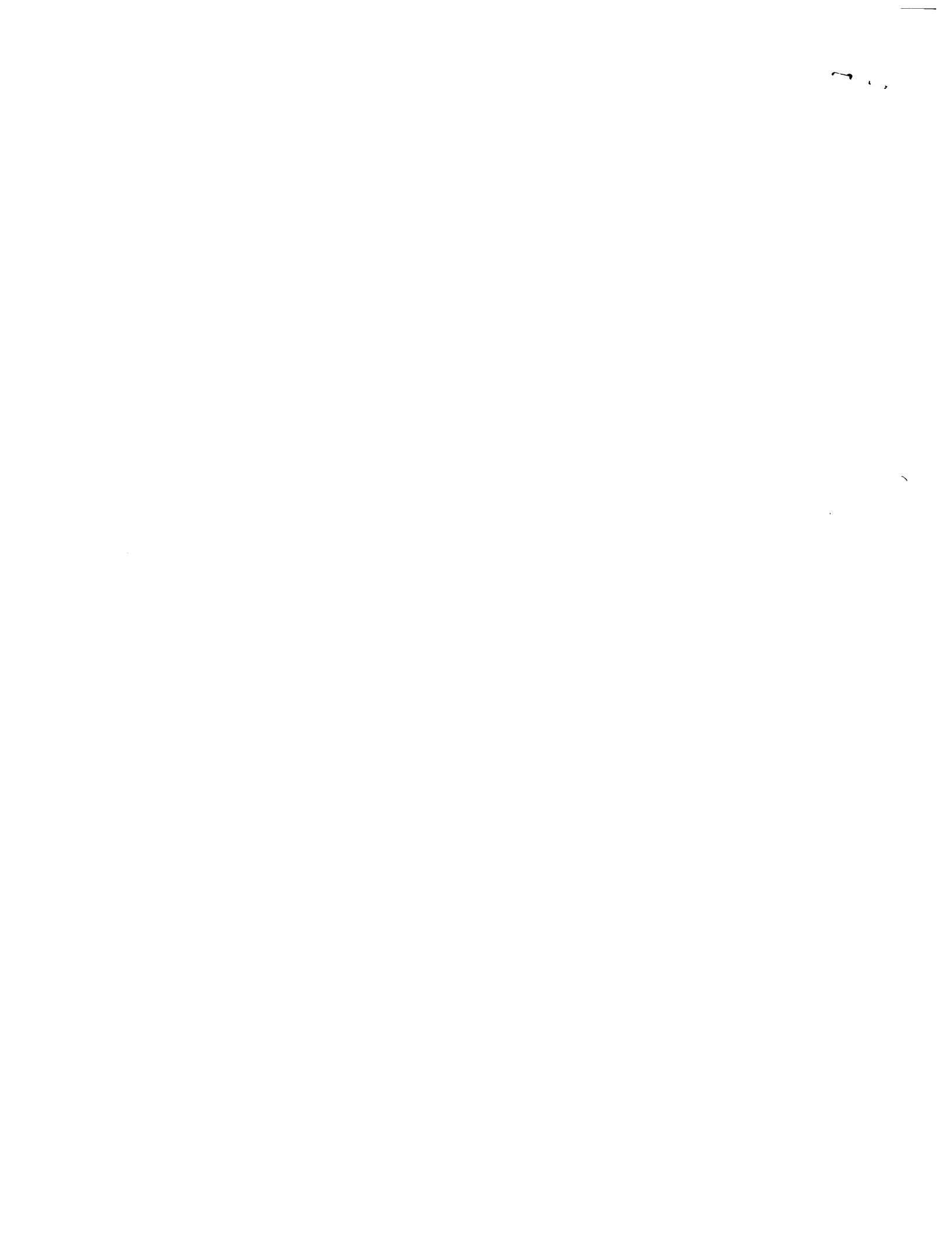


Core-shell additives of small particle size - prepd. by emulsion polymerisation, co-agglomeration, encapsulation by final shell, and isolation**Patent Assignee:** ROHM & HAAS CO; KEMPNER J S**Inventors:** ALLISON J L; KEMPNER J S; PARKER H; STEVENSON J C; WILLS M C; KEMPNER J; STEVENSON J; WILLS C M**Patent Family**

Patent Number	Kind	Date	Application Number	Kind	Date	Week	Type
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BR 9203794	A	19930427	BR 923794	A	19920929	199321	
CA 2079579	A	19930408	CA 2079579	A	19920930	199325	
US 5221713	A	19930622	US 91772406	A	19911007	199326	
JP 5247313	A	19930924	JP 92267224	A	19921006	199343	
TW 211576	A	19930821	TW 92108031	A	19921009	199347	
US 5276092	A	19940104	US 91772406	A	19911007	199402	
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US 5442012	A	19950815	US 91772406	A	19911007	199538	
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DE 69211087	E	19960704	DE 611087	A	19920930	199632	
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KR 165900	B1	19990320	KR 9218230	A	19921006	200042	
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Abstract:

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A blend of core/shell polymer particles comprises (a) an impact modifier polymer consisting of particles of (i) rubbery core, and (ii) an intermediate shell polymer; (b) a processing aid polymer component consisting of (iii) a second core particle, and one of (iv) a second intermediate crosslinked shell polymer, or (v) a third intermediate shell polymer; and (c) a shell of hard polymer encapsulating an aggregation of (a) and (b) to form a particle of at least 150 nm dia..

Particle (i) contains at least 50 wt. % derived from butadiene, 2-8C alkyl esters of acrylic acid or their mixts.; has Tg below -20 deg. C; has an average particle size below 100nm dia.; and has a wt. average molecular wt. of at least 500,000.

Intermediate (ii) contains more than 50 wt. % derived from 1-4C alkyl esters of (meth)acrylic acid; is present as 5-20 wt. % of (a); and has a glass temp. above -20 deg. C. Particle (iii) contains at least 80 wt.% derived from 4-12C alkyl ester of (meth)acrylic acid, and 0-20 pts. derived from at least one other vinyl/vinylidene monomer. Particle size is below 100nm dia. and its wt. average molecular wt. is not more than 100,000. The particle is free from units derived from graftlinking or crosslinking monomer, and is not deliberately crosslinked.

Shell polymer (iv) contains at least 90 wt. % derived from one or more vinyl aromatic monomer and/or 1-4C alkyl esters of (meth)acrylic acid and 0.5-10 wt. % derived from a monomer contg. 2 or more copolymerisable double bonds or alkali(ne earth) or transition metal salt of a copolymerizable unsatd. acid.

Shell polymer (v) contains at least 70 wt. % derived from one or more vinyl aromatic monomer or 1-4C alkyl esters of methacrylic acid. Shell (c) polymer contains more than 50 wt. % of 1-4C alkyl ester of methacrylic acid; has Tg of at least 60 deg. C and is present as 5-20 wt. % of the final core/shell blend.

USE/ADVANTAGE - PVC compsns. contg. the blends as modifying additives for extruded, injection moulded, blow-moulded and foamed articles such as window shades, protective shading, window profiles, pipe and drainage uses, appliance housings, refrigerator liners and trays and bottles for liquids/solids. Articles formed have improved toughness properties. Because of the dispersion behaviour of the blend, optical properties are improved and specific property advantages contributed by components are allowed, these including lubrication, flow and impact strength

Dwg.0/0

EP 536935 B

A blend of core/shell impact modifier polymer and core/shell processing aid polymer wherein: (a) the impact modifier polymer comprises particles of: (1) rubbery first core polymer particle having a glass temperature below -20 deg.C and an average particle size below 100 nm diameter, and containing at least 50 weight percent of units derived from butadiene, (C2 to C8)alkyl esters of acrylic acid, or mixtures thereof, and having a weight-average molecular weight of at least 500,000; and (2) first intermediate shell polymer having a glass temperature above -20 deg.C, and containing more than 50 weight percent units derived from (C1 to C4)alkyl esters of acrylic or methacrylic acid and being from 5% to 20% by weight of the core/intermediate shell impact modifier polymer particles; (b) the processing aid polymer component comprises particles of: (1) second core polymer particle having a particle size below 100 nm diameter and containing from at least 80 weight percent of units derived from (C4 to C12)alkyl esters of acrylic acid or methacrylic acid or mixtures thereof and from 0 to 20 parts of units derived from at least one other vinyl or vinylidene monomer, and having a weight-average molecular weight of no more than 100,000 and being free from units derived from graft linking or crosslinking monomer and not being deliberately crosslinked; and at least one of: (2) a second intermediate crosslinked shell polymer containing (a) at least 90 weight percent of units derived from one or more vinyl aromatic monomer and/or (C1-C4)alkyl esters of (meth)acrylic acid, (b) from 0.5 to 10 weight percent of units derived from at least one of: (i) multifunctional monomer containing two or more copolymerisable double bonds, or (ii) alkali, alkaline earth, or transition metal salt of a copolymerisable unsaturated acid; or (3) a third intermediate shell polymer containing at least 70 weight percent of units derived from one or more vinyl aromatic monomer or (C1 to C4)alkyl esters of methacrylic acid; and (c) an encapsulating shell of hard polymer having a glass temperature of at least 60 deg.C and containing more than 50% by weight of (C1 to C4)alkyl ester of methacrylic acid and being present in an amount of from 5 to 20% by weight of the final core/shell polymer blend and encapsulating an aggregation of impact modifier and processing aid particles and forming a particle of at least 150 nm diameter.

(Dwg 0/0)

US 5221713 A

An agglomerated, encapsulated blend of a core/shell impact modifier and a core/shell processing and comprising (a), (b) and (c) is new. (a) is an impact modifier component comprising particles of (1) and (2). (1) is a rubbery core polymer particle having a glass temp. below -20 deg.C and a particle size below about 100nm dia.. The rubbery core polymer particle contains at least 50 wt.% of units derived from butadiene, 2-8C alkyl esters of acrylic acid or its mixts., and has a wt. average mol. wt. of at least 500,000. (2) is an intermediate shell polymer encapsulating the rubbery core polymer and has a glass temp. above -20 deg.C. The intermediate shell contains predominately units derived from 1-4C esters of acrylic or methacrylic acid and is 5-20 of the rubber core/intermediate shell polymer particles; (b) is a processing aid component comprising particles of (1) and at least one of (2) or (3). (1) is a core polymer particle having a particle size below 100nm dia.. (1) contains at least 80 wt.% of units derived from 4-12C alkyl esters of acrylic acid or methacrylic acid or its mixts. and 0-20 pts. of units derived from at least one other vinyl or vinylidene monomer. (1) has a wt. average mol. wt. of no more than 100,000. The core polymer does not contain certain units derived from a graftlinking or crosslinking monomer and is not deliberately crosslinked. (2) is an intermediate crosslinked shell polymer encapsulating (1) and contains (a) and (b). (a) is at least 90 wt.% of units derived from one or more of vinyl aromatic monomers or 1-4C alkyl esters of (meth)acrylic acid; (b) is 0.5-10 wt.% of units derived from at least one of (i) or (ii). (i) is a multifunctional monomer contg. two or more copolymerisable double bonds; (ii) is an alkali, alkaline earth, or transition metal salt of a copolymerisable unsatd. acid. (3) is an intermediate shell stage of a polymer encapsulating (1), and, if present, (2) contains at least 70 wt.% of units derived from one or more vinyl aromatic monomers or 1-4C alkyl esters of methacrylic acid; (c) is a final encapsulating shell of hard polymer having a glass temp. of at least 60 deg.C contg. predominately units derived from a 1-4C alkyl ester of methacrylic acid. (c)

comprises 5-20 wt.% of the final core/shell polymer blend. (c) encapsulates an agglomerate of impact modifier and processing aid particles. (c) forms a particle of at least 150nm dia..

USE/ADVANTAGE - The core/shell additives are useful in modifying the processing and/or physical properties of PVC and other thermoplastic matrix polymers. (Dwg.0/0)

US5276092 The toughened composite comprises: (A) 5-40 parts of an agglomerated, encapsulated blend of a core/shell impact modifier and a core/shell processing aid contg.: (a) an impact modifier component comprising particles of: (1) a rubbery core polymer particle having a Tg under -20 deg.C. and a particle size under 100 nm diam., the rubbery core polymer particle contg. 50 wt.% or more of units derived from butadiene and/or 2-8C alkyl esters of acrylic acid, and having a wt. average MW of 500,000 or more; and (2) an intermediate shell polymer encapsulating the rubbery core polymer, having a Tg above -20 deg.C., the first intermediate shell contg. predominantly units derived from 1-4C esters of (meth)acrylic acid, and the intermediate shell being 5-20 wt.% of the rubbery core/intermediate shell polymer particles; (b) a processing aid component comprising particles of: (1) a core polymer particle having a particle size below 100 nm dia., the core polymer particle contg. 80 wt.% or more of units derived from 4-12C alkyl esters of (meth)acrylic acid or mixts. and 0-20 parts of units derived from other vinyl or vinylidene monomer(s), and having a wt. average MW of up to 100,000, the core polymer not contg. units derived from a graftlinking or crosslinking monomer, and the core polymer not being deliberately crosslinked; and one or more of: (2) an intermediate crosslinked shell polymer encapsulating the core polymer particle, and contg. (a) 90 wt.% or more of units derived from vinyl aromatic monomer(s) or 1-4C aromatic monomer(s) or 1-4C alkyl ester(s) of (b) 0.5-10 wt.% of units derived from one or more of: (i) a multifunctional monomer contg. two or more copolymerisable double bonds; or (ii) an alkali, alkaline earth, or transition metal salt of a copolymerisable unsatd. acid; (3) an intermediate shell stage of a polymer encapsulating the core polymer particle and, if present, the intermediate crosslinked shell polymer, and contg. 70 wt.% or more of units derived from vinyl aromatic monomer(s) or 1-4C alkyl ester(s) of methacrylic acid; and (c) a final external encapsulating shell of hard polymer having a Tg of 60 deg.C or higher, the encapsulating shell contg. predominantly units derived from a 1-4C alkyl ester of methacrylic acid, the encapsulating shell comprising 5-20 wt.% of the final core/shell polymer blend, the encapsulating shell encapsulating an agglomerate of impact modifier and processing aid particles, the encapsulating shell forming a particle of 150 nm diam. or more; and (b) 60-95 parts of a thermoplastic matrix resin.

USE - PVC processibility is modified using the encapsulated derivs. (Dwg.0/0)

US5442012 The prepn. of an agglomerated, encapsulated blend of a core/shell impact modifier and a core/shell processing aid comprises: (a) forming by emulsion polymerisation a rubbery core impact modifier polymer particle having a Tg below -20 deg.C and a particle size below 100 nm diam., the rubbery core polymer particle being formed from 50 wt.% or more of units derived from butadiene and/or 2-8C alkyl esters of acrylic acid, and having a wt.-average MW of 500,000 or more; (b) forming by sequential emulsion polymerisation in the presence of the rubbery core impact modifier polymer, under conditions where no new polymer particles are formed, an intermediate shell polymer encapsulating the rubbery core polymer, the intermediate shell polymer having a Tg above -20 deg.C, the intermediate shell being formed predominantly from units derived from 1-4C esters of (meth)acrylic acid, and the intermediate shell being 5-20 wt.% of the core/intermediate shell polymer particles so as to prepare the core/shell impact modifier; (c) separately forming by emulsion polymerisation a processing-aid core polymer particle having a particle size below 100 nm diam., the processing-aid core polymer particle being formed from 80 wt.% or more of units derived from 4-12C alkyl esters of (meth)acrylic acid and from 0-20 parts of units derived from other vinyl(idene) monomer(s), and having a wt.-average MW of up to 100,000, the processing-aid core polymer not contg. units derived from a graftlinking or crosslinking monomer, and the processing-aid core polymer not being deliberately crosslinked; (d) opt. forming by sequential emulsion polymerisation in the presence of the processing-aid core polymer, under conditions where no new polymer particles are formed, and encapsulating the core polymer, an intermediate crosslinked shell polymer contg.: (1) 90 wt.% or more of units derived from vinyl

aromatic monomers and/or 1-4C alkyl esters of (meth)acrylic acid, (2) 0.5-10 wt.% of units derived from one or more of: (a) a multifunctional monomer containing two or more copolymerisable double bonds, (b) a copolymerisable unsatd. acid, the copolymerisable unsatd. acid being partially to completely in the form of an alkali, alkaline earth, or transition metal salt; (e) opt. forming by sequential emulsion polymerisation in the presence of the processing-aid core polymer or the processing aid core/intermediate crosslinked shell polymer and encapsulating the processing-aid core polymer or, if present, the core/intermediate crosslinked shell polymer, under conditions where no new polymer particles are formed, an intermediate shell stage of a polymer contg. 70 wt.% or more of units derived from vinyl aromatic monomers and/or 1-4C alkyl esters of (meth)acrylic acid, where step(s) (d) or (e) must be conducted, so as to prepare the core/shell processing aid; (f) admixing the polymer particles formed in steps (a-b) and in steps (c-e) in emulsion form; (g) agglomerating the core/intermediate shell polymer particles to form a dispersion of agglomerated particles of 150 nm or more dia.; (h) forming by sequential emulsion polymerisation onto the agglomerated particles, under conditions where no new polymer particles are formed, a final external encapsulating shell of hard polymer having a Tg of 60 deg.C or more, the encapsulating shell being formed from units derived from a 1-4C alkyl ester of methacrylic acid, the encapsulating shell comprising 5-20 wt.% of the final core/shell polymer blend; and (i) isolating the final core/shell polymer blend.

USE/ADVANTAGE - Injection moulding of PVC. Handle well without compaction prior to mixing.

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(54) **Co-microagglomeration of emulsion polymers.**

(57) Core/shell additives, useful in modifying the processing and/or physical properties of poly(vinyl chloride) and other thermoplastic matrix polymers, are prepared separately at small particle sizes by emulsion polymerization, co-agglomerated, further encapsulated by a final shell, and isolated by spray-drying or coagulation. The isolated powders are readily re-dispersed to their original particle sizes in the matrix polymer.

EP 0 536 935 A1

This invention is concerned with mixtures of core/shell polymeric additives of small core particle size which are useful additives in certain thermoplastic compositions, especially polyvinyl chloride compositions, and to processes for preparing core/shell polymeric additives of small core particle size, to the core/shell additives so prepared, and to their blends with a variety of matrix thermoplastics.

5 Processing poly(vinyl chloride) into useful objects requires a variety of adjuvants such as thermal stabilizers, processing aids, lubricants, optionally impact modifiers, pigments, and the like. In recent years, polymeric additives have been developed for many of these purposes, such as impact modification by core/shell polymers based on a butadiene or poly(alkyl acrylate) core surrounded by shells containing alkyl(meth)acrylate or vinyl aromatic polymers. Also, processing aids based on high molecular polymers of alkyl methacrylates are well-known. Such processing aids aid in the conversion of the PVC particles under conditions of heat and shear to a molten plastic capable of being shaped into the final desired object, the processing aids improving the fusion behaviour and the processing of the melt. Further, special lubricating/processing aids based on polymers of alkyl (meth)acrylates have been developed which aid in fluxing and release from hot metal surfaces, further contributing relatively small increases to the melt viscosity of the PVC compound, which is important for certain processing operations, such as injection moulding.

10 The producers of such polymeric additives have continued to seek for means of combining such additives beyond simple blending, so as to obtain an unexpected improvement in properties. One means has been to form core/shell polymers wherein, for example, a lubricating polymer is encapsulated by a processing aid polymer. Such encapsulation is best accomplished by sequential emulsion polymerization under conditions where 15 the second polymer is prepared at conditions where no new particles are formed, and all the new polymer is formed at the pre-formed sites offered by the first polymer particles.

20 Simple blending of such core/shell emulsions prior to isolation, such as by coagulation or spray-drying, can create certain problems. Particles with low content of shell polymer may compact and not flow freely, or the lubricating component may deleteriously effect the fusion process, or dispersion of the additive polymers, 25 either to their initial particle size in the PVC matrix or to miscible blends with the PVC, may be adversely affected.

25 Thus the compounder of poly(vinyl chloride) has sought a means for improving the efficacy of mixtures of polymers additives, and the manufacturer has sought means to combine such more efficiently and to produce blends which handle well without compaction prior to admixture with the PVC.

30 We have now found a blend of polymeric additives which comprises a core/shell impact modifier having a core based on a polybutadiene or polyacrylate rubber and an intermediate shell of a harder polymer, i.e., one having a glass temperature above -20°C and formed mainly, i.e., from at least 50 weight percent, from C₁ to C₄ esters of (meth)acrylic acid, in combination with a processing aid component having a core formed mainly 35 from C₁ to C₄ esters of (meth)acrylic acid, optionally a second intermediate shell of polymer derived mainly from vinyl aromatic or C₁ to C₄ alkyl esters of (meth)acrylic acid and low levels of a multifunctional crosslinking monomer or an unsaturated acid partially or completely neutralized, and/or optionally with a third intermediate shell stage comprised mainly of polymers of vinyl aromatic or C₁ to C₄ esters of (meth)acrylic acid, the two 40 core-shell polymers being agglomerated together and then further encapsulated with a final shell of a polymer predominantly formed from a C₁ to C₄ ester of (meth)acrylic acid. By processing aid component is meant a polymer which aids in the processing of a matrix polymer, such as by controlling the fusion process, increasing or reducing the melt viscosity of the molten matrix polymer, preventing sticking to hot metal surfaces, increasing the melt strength, improving surface appearance, and the like. We further have discovered a process for preparing such an agglomerated, encapsulated blend, and a blend with a thermoplastic matrix polymer, such as 45 PVC, of such a blend.

45 Most specifically, our invention comprises a blend of a first core/shell impact modifier and a second core/shell processing aid which comprises:

(a) an impact modifier component comprising particles of:

50 (1) a rubbery first core polymer particle having a glass temperature below about -20°C and a particle size below about 100 nm diameter, the first core polymer particle being formed from at least 50 weight percent of units derived from butadiene, C₂ to C₈ lower alkyl esters of acrylic acid, or mixtures thereof, and having a weight-average molecular weight of at least about 500,000;

(2) a first intermediate shell polymer having a glass temperature above -20°C, the first intermediate shell being formed predominantly from units derived from C₁ to C₄ esters of acrylic or methacrylic acid, and the first intermediate shell being from about 5% to about 20% by weight of the first 55 core/intermediate shell polymer particles;

(b) a processing aid component comprising particles of:

(1) a second core polymer particle having a particle size below about 100 nm diameter, the second core polymer particle being formed from at least 80 weight percent of units derived from C₄ to C₁₂ alkyl

esters of acrylic acid or methacrylic acid or mixtures thereof and from 0 to about 20 parts of units derived from at least one other vinyl or vinylidene monomer, and having a weight-average molecular weight of no more than about 100,000, the second core polymer not containing units derived from a graftlinking or crosslinking monomer, and the second core polymer not being deliberately crosslinked; and at least one of:

5 (2) a second intermediate crosslinked shell polymer containing

- (a) at least about 90 weight percent of units derived from one or more of vinyl aromatic monomers, such as styrene, or C_1 - C_4 alkyl esters of (meth)acrylic acid, such as methyl methacrylate or butyl acrylate,
- 10 (b) from about 0.5 to about 10 weight percent of units derived from at least one of:
 - (i) a multifunctional monomer containing two or more copolymerizable double bonds;
 - (ii) an alkali, alkaline earth, or transition metal salt of a copolymerizable unsaturated acid, and optionally units derived from the copolymerizable unsaturated acid; or
- (3) a third intermediate shell stage of a polymer containing at least about 70 weight percent of units derived from one or more of vinyl aromatic monomers or C_1 - C_4 alkyl esters of methacrylic acid;
- 15 (c) an encapsulating shell of hard polymer having a glass temperature of at least 60°C, the encapsulating shell being formed predominantly from units derived from a C_1 to C_4 alkyl ester of methacrylic acid, the encapsulating shell comprising from about 5 to about 20% by weight of the final core/shell polymer blend, the encapsulating shell encapsulating an aggregation of impact modifier and processing aid particles, the encapsulating shell forming a particle of at least 150 nm diameter.

20 In the above description the processing aid component must contain at least one of the two optional intermediate shells. If both are present, then the formation of the second intermediate shell must precede the formation of the third intermediate shell.

25 The presence of the second optional shell may add to the impact strength of the resulting blend, especially when comprised of units derived from esters of acrylic acid.

The blend may further contain at least one of an antioxidant or a thermal stabilizer, such as those needed to stabilize the blend during isolation by coagulation and spray-drying, or during the processing of the blend with a thermoplastic matrix resin. Such stabilizers may include antioxidants such as hindered phenols, thermal stabilizers such as disulfides, mercaptoesters, and the like, or organic phosphites, such as trisarylphosphites and the like.

30 For best compatibility with many thermoplastic matrix resins, such as PVC, it is preferred that at least one of the encapsulating shell of the final core/shell polymer blend, the first intermediate shell polymer, or the third intermediate shell stage of the second core/shell polymer comprises a majority of units derived from methyl methacrylate. Thus, these shells may contain a homopolymer of methyl methacrylate, or copolymers of methyl methacrylate with up to about 50%, preferably up to about 20%, of at least one co-monomer such as ethyl acrylate, butyl acrylate, butyl methacrylate, styrene, acrylonitrile, and the like.

35 In the rubbery core of the impact modifier component, for ease of preparation, especially by emulsion polymerization, it is preferred that the core be predominantly at least one of butadiene or of butyl acrylate. Especially preferred, for reasons of producing weatherable impact modifiers, is a homopolymer of butyl acrylate.

40 For best impact properties, it is preferred that the rubbery first core polymer, especially if formed from an acrylate monomer such as butyl acrylate or 2-ethylhexyl acrylate, further contains units derived from at least one multiunsaturated monomer, such as at least one of allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate divinylbenzene, a di- or triacrylate ester of a polyol, or a di- or trimethacrylate ester of a polyol, and the like.

45 The first core/shell impact modifier may contain additional shells between core and first intermediate shell or external to the first intermediate shell, such as polymers of styrene for improvement of refractive index, as long as the other requirements of the first core/shell polymer are met.

50 In the processing aid portion of the blend, for reasons of cost and efficacy it is preferred that the C_4 to C_{12} alkyl ester of acrylic acid or methacrylic acid in the second core polymer particle is butyl acrylate. Such core polymers can include homopolymers of butyl acrylate, copolymers of butyl acrylate with other acrylates, such as ethyl acrylate, 2-ethylhexyl acrylate and the like, copolymers with monomers of higher refractive index, such as styrene and the like, copolymers with acrylonitrile and the like. The second core polymer may be effectively reduced in molecular weight by use of chain transfer agents, such as alkyl mercaptans.

55 The second stage of the processing aid may be formed from homo- or copolymers of monomers such as styrene, methyl methacrylate, butyl acrylate, ethyl acrylate, and the like. This stage is either crosslinked by the presence of a multifunctional monomer containing two or more double bonds, such as from about 0.1 to about 5% of at least one of allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, divinylbenzene, a di- or triacrylate ester of a polyol, or a di- or trimethacrylate ester of a polyol.

Alternatively or concurrently, the second stage of the processing aid may be crosslinked by ionic groups, which crosslinking may be thermally reversible. Such may be accomplished by use of an unsaturated acid, preferably one of methacrylic acid, acrylic acid, itaconic acid, maleic acid, fumaric acid, alpha-methylene-delta-methyladipic acid, or acryloxypropionic acid. The salt may be alkali, such as sodium, potassium, and the like, 5 alkaline earth, such as calcium and the like, or transition metal, such as zinc and the like. Preferred is the sodium salt. Neutralization may be partial or complete.

Our invention further contemplates a toughened blend of the blend of first core/shell impact modifier and second core/shell processing aid described above with a thermoplastic matrix resin. More specifically, after 10 isolation, the impact modifier/processing aid additive may be mixed with the appropriate matrix polymer at levels to obtain improvement in impact, which will generally be from about 3 to about 40 percent by weight of the toughened blend. The thermoplastic resin or matrix or polymer of the toughened blend may be one or more of many well-known thermoplastics known to accept impact modification from core/ shell modifiers. The thermoplastic resin may be a homopolymer of vinyl chloride, a copolymer containing at least 80 weight percent of 15 units derived from vinyl chloride, such as a vinyl chloride-vinyl acetate copolymer, a homopolymer of methyl methacrylate or a copolymer containing at least 80 weight percent of units derived from methyl methacrylate, such as a methyl methacrylate/ethyl acrylate or a methyl methacrylate/ styrene copolymer. The thermoplastic resin may be an engineering resin, such as a polyester of terephthalic acid and an aliphatic glycol, a polyamide, a polycarbonate, a polyglutarimide, an acrylonitrile-butadiene-styrene resin, or a blend of at least two of such resins.

20 Because of the thinness of the final encapsulating shell and because it is often selected to be readily dispersible in the matrix polymer, on processing with heat and shear, the co-agglomerated polymer will usually be dispersed into domains of particle size equivalent to those of the particles of the non-aggregated core/intermediate shell polymers. This dispersion behaviour is advantageous for improvement of optical properties of the blend as well as allowing the specific property advantages contributed by the various components, 25 such as lubrication, improved flow, impact strength, and the like, to be realized after the blend is fused. In the presence of the processing aid component of the impact modifier/ processing aid blend, processing of the matrix polymer is improved. For PVC, certain processing additives, such as those based on a core of low molecular weight polymers of butyl acrylate, will aid in release of the PVC from hot metal surfaces aid in reducing the melt viscosity of the blend towards improved injection moulding.

30 The toughened blend may further contain one or more of lubricant, processing aid, rheology modifier, dye, pigment, flame retardant, thermal stabilizer, antioxidant, antiozonant, ultraviolet stabilizer, mould release agent, reinforcing filler or non-reinforcing filler. The reinforcing filler may be least one of glass fibres, glass spheres, talc, or mica.

35 In the case of poly(vinyl chloride), the blend may also contain a heat distortion improver, such as a polyglutarimide. The impact modifier may be used in PVC with conventional stabilizers which may be selected depending on the degree of stability, colour retention, lubricity, and weatherability required, such as organotin, organic lead, barium-cadmium, and calcium-zinc stabilizers.

40 The PVC blends containing the impact modifiers of the present invention may be used for production of extruded, injection moulded, blow-moulded and foamed articles of commerce, such as siding, especially for architectural uses, window shades, protective shading, window profiles, pipe and drainage uses, appliance housings, refrigerator liners and trays, bottles for packaging of liquids and solids, such as potable water, food oils, and the like, and for many other conventional uses.

45 The blends with engineering resins, such as a polyester of terephthalic acid and an aliphatic glycol, a polyamide, a polycarbonate, a polyglutarimide, an acrylonitrile-butadiene-styrene resin, or a blend of at least two of such resins, may be used for many applications where the engineering resin is already employed, but where further toughness is required, such as appliance housings, automotive parts, food packaging, such as trays, bottles, and the like, toys, furniture, and other well-known uses.

Blends with methyl methacrylate may be employed to give additional toughness to uses such as capstock, translucent or transparent glazing, moulded articles, such as cups, taillights, and the like.

50 The invention further encompasses the novel process for preparing a blend of a first core/shell impact modifier and a second core/shell processing aid which comprises:

55 (a) forming by emulsion polymerization a rubbery first core polymer particle having a glass temperature below about -20°C and a particle size below about 100 nm diameter, the first core polymer particle being formed from at least 50 weight percent of units derived from butadiene, C₂ to C₈ alkyl esters of acrylic acid, or mixtures thereof, and having a weight-average molecular weight of at least about 500,000;

(b) forming by sequential emulsion polymerization in the presence of the first core polymer, under conditions where essentially no new polymer particles are formed, a first intermediate shell polymer having a glass temperature above -20°C, the first intermediate shell being formed predominantly from units de-

rived from C₁ to C₄ esters of acrylic or methacrylic acid, and the first intermediate shell being from about 5% to about 20% by weight of the first core/intermediate shell polymer particles;

(c) separately forming by emulsion polymerization a second core polymer particle having a particle size below about 100 nm diameter, the second core polymer particle being formed from at least 80 weight percent of units derived from C₄ to C₁₂ alkyl esters of acrylic acid or methacrylic acid or mixtures thereof and from 0 to about 20 parts of units derived from at least one other vinyl or vinylidene monomer, and having a weight-average molecular weight of no more than about 100,000, the second core polymer not containing units derived from a graftlinking or crosslinking monomer, and the second core polymer not being deliberately crosslinked;

10 (d) optionally forming by sequential emulsion polymerization in the presence of the second core polymer, under conditions wherein essentially no new polymer particles are formed, a second intermediate cross-linked shell polymer containing

(1) at least about 90 weight percent of units derived from one or more of vinyl aromatic monomers or C₁ to C₄ alkyl esters of (meth)acrylic acid,

15 (2) from about 0.5 to about 10 weight percent of units derived from at least one of:

(a) a multifunctional monomer containing two or more copolymerizable double bonds;
(b) a copolymerizable unsaturated acid, the copolymerizable unsaturated acid being partially to completely in the form of an alkali, alkaline earth, or transition metal salt;

20 (e) optionally forming by sequential emulsion polymerization in the presence of the second core/intermediate crosslinked shell polymer, under conditions wherein essentially no new polymer particles are formed, a third intermediate shell stage of a polymer containing at least about 70 weight percent of units derived from one or more of vinyl aromatic monomers or C₁ to C₄ alkyl esters of methacrylic acid, wherein at least one steps (d) or (e) must be conducted;

(f) admixing the polymer particles formed in steps (a-b) and in steps (c-e) in emulsion form;

25 (g) aggregating the core/intermediate shell polymer particles to form a dispersion of aggregated particles of at least 150 nm diameter;

(h) forming by sequential emulsion polymerization onto the aggregated particles, under conditions wherein essentially no new polymer particles are formed, an encapsulating shell of hard polymer having a glass temperature at least 60°C, the encapsulating shell being formed predominantly from units derived from a C₁ to C₄ alkyl ester of methacrylic acid, the encapsulating shell comprising from about 5 to about 20% by weight of the final core/shell polymer blend; and

(i) isolating the final core/shell polymer blend.

30 The conditions by which the various polymerizations are run are generally known to the art of core/shell emulsion polymerization. The initiators are those common to emulsion polymerization, such as persulfates, peresters, hydroperoxides, peracids, azo compounds, and the like, and some or all of the initiators may be combined with activators to form "redox" pairs. Such activators include sodium formaldehyde sulfoxylate, sodium metabisulfite, sodium hydrosulfite, and the like.

35 Surfactants may be chosen from a variety known to the emulsion art, such as alkali metal or ammonium salts of long-chain alkylsulfonic acids, long-chain alkylsulfates, derivatives of aromatic sulfonates, ethoxylated alkaryl phosphates, and the like. To accomplish the microagglomeration, it appears necessary that the emulsifier be the alkali metal or tetrasubstituted ammonium salt of a strong acid, and that emulsifiers based on weak acids, such as salts of fatty acids, are less effective. Preferred are sulfates and sulfonates, such as sodium lauryl sulfate, sodium dodecylbenzene sulfonate, potassium dodecylbenzene sulfonate, lauryl(ethoxy)sulfates and sulfonates, lauryl(polyethoxy)sulfates and sulfonates, alkaryl(polyethoxy)sulfates and sulfonates, and the like. It further appears that the microagglomeration is most effective when the particle size of the starting polymers are below about 100 nm.

40 The microagglomerations may be conducted by addition of appropriate coagulants in limited amounts so as to bring the particles together without a total precipitation from the latex. Such can be accomplished by careful addition of salts such as sodium chloride, calcium chloride, and the like, or if the emulsion is stabilized with a soap with carboxylic acid groups, by addition of an appropriate acid. An effective means is to add separate streams of a weak acid and a weak base with rapid stirring so that the salt is formed in situ in a diluted form. The weak acid and weak base may be added as concentrated solutions, so the emulsion is diluted very little during the agglomeration step.

45 The weak acid and weak base should be water-soluble, and it is preferred that their salt be also. Suitable weak bases are ammonia, low molecular weight amines such as monomethyl amine, and the like. Ammonia is preferred. Suitable weak acids are carbon dioxide, sulfur dioxide, acetic acid, formic acid, propionic acid, and the like. Acetic acid is preferred.

50 On agglomerating the mixed latex of first core/intermediate shell polymer particles to form a latex

of co-agglomerated particles of at least 150 nm diameter, the solids content of the latex of first core/intermediate shell polymer particles should be no higher than about 40 percent, and if the addition method utilizing separate streams of a weak acid and a weak base be utilized, no higher than about 30%, and the solids content of the latex of agglomerated particles should be no higher than about 30%. Otherwise the mixtures

5 become so viscous that stirring can be disturbed and effective agglomeration cannot occur.

The impact modifier/processing aid further comprises a final encapsulating shell of hard polymer of glass temperature at least 60°C, the final encapsulating shell being formed predominantly from units derived from methyl methacrylate, the final encapsulating shell comprising from about 5 to about 20% by weight of the core/ shell impact modifier, the final encapsulating shell encapsulating more than one core/intermediate shell particles, and the final encapsulating shell forming a particle of at least 150 nm diameter. The encapsulation process again is conducted under conditions where the amount of free encapsulating polymer is minimized, that is, with no additional soap and under conditions known to the art for encapsulation in conventional core/shell modifiers. Thus the final encapsulating shell may be a homopolymer of methyl methacrylate, a copolymer of methyl methacrylate with a small amount of an alkyl acrylate or an alkyl methacrylate, such as ethyl methacrylate or butyl acrylate, a copolymer of methyl methacrylate with styrene, a copolymer of methyl methacrylate with methacrylic acid, and the like, as long as the methyl methacrylate is greater than 50% by weight of the intermediate shell polymer. The final encapsulating shell polymer may be partially or totally attached to or grafted to the core polymers, but it is preferred that it not be highly grafted or attached. It is further preferred that the molecular weight of the final encapsulating polymer be of relatively high molecular weight, such as above about 100,000. Molecular weights which are very high, such as about 1,000,000 and above, of the final encapsulating polymer are difficult to obtain without attachment or grafting to the core or intermediate shell. Nevertheless, certain compositions having a quite high molecular weight of the final encapsulating shell may be useful for certain applications. The low level of final encapsulating shell polymer is chosen so as to dilute the rubber and processing aid component content as little as possible whilst still allowing isolation of the impact modifier with acceptable isolation rates and flow properties.

10 The total rubber (first core polymer) and second core polymer content of the modifier after final encapsulation preferably should be no more than about 86%, or effective redispersion is more difficult to accomplish, which would lead, e.g., to a blend of modifier with PVC of poorer light transmission. This means that the total of all shell polymers should preferably be at least about 14 weight percent of the total core/shell polymer.

15 The most unusual attribute of the new modifier is that the final shell encapsulates more than one particle. After the initial smaller particles are agglomerated, the final shell then can encompass several original particles within one shell. It is preferred that the final shell encapsulate at least ten of the original particles. The number of original particles encapsulated can be calculated from the geometry relationships of the initial core/intermediate shell particle, in that the volume of the final core/shell polymer will be approximately 20 $(D_a/D_p)^3 + 3$ that of the core/intermediate shell particle, where D_a and D_p are the measured diameters of the core/ intermediate shell particle and of the agglomerated core/ intermediate shell/final shell particle, respectively.

25 The polymeric additive may be isolated from emulsion by any of several well-known means. It may be admixed with hot matrix polymer on a mill or in an intensive mixer whilst still in emulsion form and the water flashed off. It is preferred it be separately isolated by conventional means, such as spray-drying, freeze-coagulation, salt-coagulation, such as by addition of an aqueous solution of a salt of an inorganic acid, such as sodium chloride, magnesium acetate, calcium hypophosphite, and the like, methanol-coagulation, and the like, and then dried. It is preferred not to dry the polymeric additive at temperatures which may fuse the modifier and delay redispersion, such- as by pelletization by means of an extruder, although such methods may be used if conditions which avoid fusion are chosen. In addition to the specific embodiments of this invention illustrated below, we contemplate equivalents of the blends of this invention wherein in addition to the specific units taught, additional units may be present which do not adversely affect the utility and properties of this invention. Such equivalent blends can be prepared in a conventional manner, e.g., by substituting in addition a corresponding monomer bearing a different or additional substituent as starting material in the reactions described in the following preparative Examples.

Example 1 Microagglomerated Acrylic Impact Modifier Latex Polymer

A. Small Particle Size Acrylic Impact Modifier

1. First core/first intermediate shell

55 In a 5-litre round bottom flask, 1179 grams deionized water was heated to 55°C with nitrogen sparge. At

55°C, the nitrogen sparge is changed to a constant sweep. Then the following solutions are added to the flask: 17.52 grams of a 0.125 weight % sodium p-nitrosophenolate solution with 7.47 grams deionized rinse water, 15.22 grams of 1.44 weight % tartaric acid solution with 3.46 grams rinse water and 36.18 grams of 25 weight % sodium lauryl sulfate solution with 29.5 grams of rinse water. A separated emulsified monomer mixture is prepared containing 280.7 grams water, 7.62 grams 25% sodium lauryl sulfate solution, 1087.4 grams n-butyl acrylate and 7.68 grams allyl methacrylate. This emulsified monomer mixture is polymerized in 4 separate shots. The first shot contains 153.7 grams of this monomer emulsion mixture. After it is added to the flask, 0.20 grams 70% t-butyl hydroperoxide and 1.1 grams sodium sulfoxylate formaldehyde dissolved in 17.35 grams of water are immediately added to the flask. Five grams of water are used to rinse the container for sodium sulfoxylate formaldehyde and 104 grams of water is used to rinse the container for the monomer emulsion. After the exotherm has reached its peak temperature, the reaction mixture is held at this peak temperature for 15 minutes and then cooled to 53°C. The second shot of monomer emulsion, 127.45 grams, is now added into the flask followed by another addition of 0.15 grams of the 70% t-butyl hydroperoxide solution. After the exotherm, the mixture is held at the peak temperature for 15 minutes and then cooled to 53°C. The third charge of monomer emulsion is 573.6 grams of the total monomer mixture. The third addition of the initiator is 0.70 grams of the 70% t-butyl hydroperoxide. The reaction is allowed to exotherm and is held at the peak temperature for 15 minutes. Then the mixture is cooled to 57°C. The last addition of the monomer mixture is 573.6 grams and the last t-butyl hydroperoxide solution addition is 0.70 grams. Then 1025 grams water are used to rinse the emonomer emulsion container. Three minutes after the exotherm peak temperature, 0.18 grams of t-butyl hydroperoxide solution and 0.12 grams sodium sulfoxylate formaldehyde dissolved in 7.46 grams of water are added to the reaction mixture followed by an one hour holding at the peak temperature. The emulsion is then cooled to 53°C. The polymer solids content is 28.9%.

To the above emulsion is then added 5.33 grams of 25% sodium lauryl sulfate solution and 15 grams of water. Another 20 grams of water is used to rinse the container. After this mixture is stirred for 15 minutes, 149.3 grams of methyl methacrylate and 0.58 grams of n-dodecyl mercaptan are charged to the reaction flask followed by 100 grams of a water rinse of the monomer container. Then 0.22 grams of sodium sulfoxylate formaldehyde dissolved in 20 grams of water and 0.22 grams of sodium persulfate dissolved in 120 grams of water are added. After the exotherm peak temperature, the residual monomer is further reacted by adding 0.08 grams of sodium sulfoxylate formaldehyde in 20 grams of water and 0.08 grams of sodium persulfate in 20 grams of water. One hour after this addition, the solid content is found to be 29.9%. The latex particle size is 76 nm. This is Latex A-1 in Example 3.

2. Microagglomeration

In a 5000 ml four neck round bottom flask, which is equipped with a stirrer, a thermometer and a condenser, 3000 grams small particle size impact modifier latex obtained in the above described procedure are heated to 90°C. The agglomerating agents are concentrated ammonia (29.3% by weight) and acetic acid (50% by weight) used as two separate solutions. To the stirred emulsion at 90°C, ammonia and acetic acid solutions are added alternately in 1.19 ml and 2.14 ml increments every 5 minutes. The latex particle size is measured after each addition. The agglomeration process is stopped when the desired particle size is achieved (usually 200 - 250 nm). The agglomerated latex is then cooled to 53°C.

3. Encapsulation by Methyl Methacrylate

Under nitrogen sweep, 7.14 grams 28% sodium lauryl sulfate solution, 100 grams of methyl methacrylate and 0.4 grams of n- dodecyl mercaptan are added to the above agglomerated emulsion. 214 grams water is used to rinse the containers for the added materials. After the mixture is stirred for 10 minutes, 0.15 grams sodium sulfoxylate formaldehyde dissolved in 10 grams water and 0.15 grams sodium persulfate dissolved in 10 grams water are added to the reaction mixture. After an exotherm is observed, the residual monomer is further reacted by addition of 0.05 grams sodium sulfoxylate formaldehyde which is dissolved in 4 grams of water and 0.05 grams sodium persulfate which is dissolved in 4 grams of water. The final emulsion is held at 55°C for 1 hour and then cooled to room temperature.

4. Coagulation of the Microagglomerated Acrylic Impact Modifier

In a 4000 ml beaker, 2000 grams 0.475 % calcium chloride solution is heated to 85°C. Under agitation, 1000 grams of the above encapsulated emulsion is slowly poured into the calcium chloride solution. The mixture is allowed to be stirred for 15 minutes and then filtered to remove water. The wet coagulum is washed

with 1500 grams water and filtered to remove water. The coagulated polymer is dried in a fluid bed dryer at 80°C.

Example 2 Microagglomerated Viscosity Reducing Additive

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Small Particle Size Acrylic Viscosity Reducing Additive

In a 5-litre round bottom flask, 1179 grams deionized water was heated to 55°C with nitrogen sparge. At 55°C, the nitrogen sparge is changed to a constant sweep. Then the following solutions are added to the flask: 17.52 grams of a 0.125 weight % sodium p-nitrosophenolate solution with 7.47 grams deionized rinse water, 15.22 grams of 1.44 weight % tartaric acid solution with 3.46 grams rinse water and 32.29 grams of 28 weight % sodium lauryl sulfate solution with 29.5 grams of rinse water. A separate emulsified monomer mixture is prepared containing 280.7 grams water, 6.82 grams 28% sodium lauryl sulfate solution, 1087.4 grams n-butyl acrylate and 10.87 grams n-dodecyl mercaptan. This emulsified monomer mixture is polymerized in 4 separate shots. The first shot contains 153.7 grams of this monomer emulsion mixture. After it is added to the flask, 0.20 grams 70% t-butyl hydroperoxide and 1.1 grams sodium sulfoxylate formaldehyde dissolved in 17.35 grams of water are immediately added to the flask. Five grams of water are used to rinse the container for sodium sulfoxylate formaldehyde and 104 grams of water is used to rinse the container for the monomer emulsion. After the exotherm has brought the mixture to peak temperature, the reaction mixture is held at this peak temperature for 15 minutes and then cooled to 53°C. The second shot of monomer emulsion, 127.45 grams, is now added into the flask followed by another addition of 0.15 grams of the 70% t-butyl hydroperoxide solution. After the exotherm, the mixture is held at the peak temperature for 15 minutes and then cooled to 53°C. The third charge of monomer emulsion is 573.6 grams of the total monomer mixture. The third addition of the initiator is 0.70 grams of the 70% t-butyl hydroperoxide. The reaction is allowed to exotherm and is held at the peak temperature for 15 minutes. Then the mixture is cooled to 57°C. The last addition of the monomer mixture is 573.6 grams and the last t-butyl hydroperoxide solution addition is 0.70 grams. Then 1025 grams water are used to rinse the monomer emulsion container. Three minutes after the exotherm peak temperature, 0.18 grams of t-butyl hydroperoxide solution and 0.12 grams sodium sulfoxylate formaldehyde dissolved in 7.46 grams of water are added to the reaction mixture, followed by a one hour hold at the peak temperature. The emulsion is then cooled to 53°C. The polymer solids content is 28.9%.

To the above emulsion is added 5.33 grams of 25% sodium lauryl sulfate solution and 15 grams of water. Another 20 grams of water is used to rinse the container. After this mixture is stirred for 15 minutes, 274 grams of methyl methacrylate and 2.74 grams of n-dodecyl mercaptan are charged to the reaction flask followed by a 100 grams water rinse of the monomer container. Then 0.421 grams of sodium sulfoxylate formaldehyde dissolved in 20 grams of water and 0.41 grams of sodium persulfate dissolved in 120 grams of water are added. After the exotherm peak temperature, the residual monomer is further reacted by adding 0.14 grams of sodium sulfoxylate formaldehyde in 20 grams of water and 0.14 grams of sodium persulfate in 20 grams of water. One hour after this addition, the solid content is found to be 32 %. This is latex B-1 in Example 3.

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Microagglomeration

In a 1000 ml four neck round bottom flask, which is equipped with a stirrer, a thermometer and a condenser, 750 grams small particle size viscosity reducing additive latex obtained in the above described procedure are heated to 90°C. The agglomerating agents are concentrated ammonia (29.3% by weight) and acetic acid (50% by weight) used as two separate solutions. To the 90°C stirred emulsion, ammonia and acetic acid solutions are added alternately in 0.30 ml and 0.54 ml increment every 5 minutes. The latex particle size is measured after each addition. The agglomeration process is stopped when the desired particle size is achieved (usually 200 - 250 nm). The agglomerated latex is mixed with 8.03 grams 28% sodium lauryl sulfate solution and then cooled to 53°C.

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Encapsulation by Methyl Methacrylate

Under nitrogen sweep, 1.79 grams 28% sodium lauryl sulfate solution, 25 grams of methyl methacrylate and 0.1 grams of n- dodecyl mercaptan are added to the above agglomerated emulsion. 54 grams water is used to rinse the containers for the added materials. After the mixture is stirred for 10 minutes, 0.0375 grams sodium sulfoxylate formaldehyde dissolved in 10 grams water and 0.0375 grams sodium persulfate dissolved in 10 grams water are added to the reaction mixture. After an exotherm is observed, the residual monomer is further reacted by addition of 0.012 grams sodium sulfoxylate formaldehyde which is dissolved in 4 grams of

water and 0.012 grams sodium persulfate which is dissolved in 4 grams of water. The final emulsion is held at 55°C for 1 hour and then cooled to room temperature.

Coagulation of the Microagglomerated Viscosity Reducing Additive

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In a 4000 ml beaker, 1667 grams 0.475 % calcium chloride solution is heated to 85°C. Under agitation, 833 grams of the above encapsulated emulsion is slowly poured into the calcium chloride solution. The mixture is stirred for 15 minutes and then filtered to remove water. The wet coagulum is washed with 1250 grams water and filtered to remove water. The coagulated polymer is dried in a fluid bed dryer at 80°C. This is Polymer B in the following examples.

Example 3 Co-microagglomerated Acrylic Impact modifier and Viscosity Reducing Additive

15 This example presents the co-microagglomeration of the two core/ intermediate shell latices followed by encapsulation with a final shell.

Small Particle Size Acrylic Impact Modifier

20 Same as the small particle size acrylic impact modifier in Example A (Latex A-1).

Small Particle Size Viscosity Reducing Additive

25 Same as the small particle size viscosity reducing additive in Example B (Latex B-1).

25 Co-microagglomeration

30 In a 5000 ml four neck round bottom flask, which is equipped with a stirrer, a thermometer and a condenser, 2000 grams small particle size impact modifier latex A-1 obtained by the procedure described in Example 1 and 2000 grams small particle size viscosity reducing additive latex B-1 prepared by the procedure described in Example 2 are heated to 90°C. The agglomerating agents are concentrated ammonia (29.3% by weight) and acetic acid (50% by weight) used as two separate solutions. To the 90°C stirred emulsion, ammonia and acetic acid solutions are added alternately in 1.58 ml and 2.86 ml increments every 5 minutes. The latex particle size is measured after each addition. The agglomeration process is stopped when the desired particle size (263 nm) is achieved. The agglomerated latex is mixed with 42.9 grams of 28% sodium lauryl sulfate solution, then cooled to 53°C.

Encapsulation by Methyl Methacrylate

40 Under nitrogen sweep, 9.05 grams 28% sodium lauryl sulfate solution, 126.7 grams of methyl methacrylate and 0.51 grams of n- dodecyl mercaptan are added to the above agglomerated emulsion. 275 grams water is used to rinse the containers for the added materials. After the mixture is stirred for 10 minutes, 0.19 grams sodium sulfoxylate formaldehyde dissolved in 12 grams water and 0.19 grams sodium persulfate dissolved in 12 grams water are added to the reaction mixture. After an exotherm is observed, the residual monomer is further reacted by addition of 0.06 grams sodium sulfoxylate formaldehyde which is dissolved in 4 grams of water and 0.06 grams sodium persulfate which is dissolved in 4 grams of water. The final emulsion is held at 55°C for 1 hour and then cooled to room temperature.

Coagulation of the co-microagglomerated Acrylic Impact Modifier and Viscosity

50 Reducing Additive

55 In a 4000 ml beaker, 2000 grams 0.475 % calcium chloride solution is heated to 99°C. Under agitation, 1000 grams of the above encapsulated emulsion is slowly poured into the calcium chloride solution. The mixture is stirred for 15 minutes and then filtered to remove water. The wet coagulum is washed with 1500 grams water and filtered to remove water. The coagulated polymer is dried in a fluid bed dryer at 80°C. This is Polymer C in the following text.

Example 4 Microagglomerated Encapsulated Viscosity Reducing Additive

This example presents a core/shell polymer with a crosslinked intermediate stage, and the microagglomeration/encapsulation in the absence of an impact modifier.

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Small Particle Size Acrylic Impact Modifier

In a 5-litre round bottom flask, 1179 grams deionized water was heated to 55°C with nitrogen sparge. At 55°C, the nitrogen sparge is changed to a constant sweep. Then the following solutions are added to the flask: 17.52 grams of a 0.125 weight % sodium p-nitrosophenolate solution with 7.47 grams deionized rinse water, 15.22 grams of 1.44 weight % tartaric acid solution with 3.46 grams rinse water and 32.29 grams of 28 weight % sodium lauryl sulfate solution with 29.5 grams of rinse water. A separated emulsified monomer mixture is prepared containing 172.7 grams water, 4.18 grams 28% sodium lauryl sulfate solution, 664.6 grams n-butyl acrylate and 6.66 grams n-dodecyl mercaptan. This emulsified monomer mixture is polymerized in 3 separate shots. The first shot contains 153.7 grams of this monomer emulsion mixture. After it is added to the flask, 0.20 grams 70% t-butyl hydroperoxide and 1.1 grams sodium sulfoxylate formaldehyde dissolved in 17.35 grams of water are immediately added to the flask. Five grams of water are used to rinse the container for sodium sulfoxylate formaldehyde and 104 grams of water is used to rinse the container for the monomer emulsion. After the exotherm has reached its peak temperature, the reaction mixture is held at this peak temperature for 15 minutes and then cooled to 53°C. The second shot of monomer emulsion, 122.98 grams, is now added into the flask followed by another addition of 0.15 grams of the 70% t-butyl hydroperoxide solution. After the exotherm, the mixture is held at the peak temperature for 15 minutes and then cooled to 53°F. The third charge of monomer emulsion is 571.5 grams of the total monomer mixture. The third addition of the initiator is 0.70 grams of the 70% t-butyl hydroperoxide. The reaction is allowed to exotherm and is held at the peak temperature for 15 minutes. Then the mixture is cooled to 57°C. A second monomer emulsion mixture is prepared containing 108 grams of water, 2.64 grams of 28% sodium lauryl sulfate, 418.43 grams of n-butyl acrylate and 2.93 grams of allyl methacrylate. This mixture is added to the reaction flask together with 0.70 grams 70% t-butyl hydroperoxide solutions. Then 1025 grams water is used to rinse the monomer emulsion container. Three minutes after the exotherm peak temperature, 0.18 grams of t-butyl hydroperoxide solution and 0.12 grams sodium sulfoxylate formaldehyde dissolved in 7.46 grams of water are added to the reaction mixture followed by an one hour holding at the peak temperature. The emulsion is then cooled to 53°C. The polymer solids content is 29 %.

30

To the above emulsion are added 5.33 grams of 25% sodium lauryl sulfate solution and 15 grams of water. Another 20 grams of water is used to rinse the container. After this mixture is stirred for 15 minutes, 149.32 grams of methyl methacrylate and 0.58 grams of n-dodecyl mercaptan are charged to the reaction flask followed by a 100 grams water rinse of the monomer container. Then 0.22 grams of sodium sulfoxylate formaldehyde dissolved in 20 grams of water and 0.22 grams of sodium persulfate dissolved in 120 grams of water are added. After the exotherm peak temperature, the residual monomer is further reacted by adding 0.08 grams of sodium sulfoxylate formaldehyde in 20 grams of water and 0.08 grams of sodium persulfate in 20 grams of water. One hour after this addition, the solid content is found to be 30%. This is latex D-1.

Microagglomeration

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In a 1000 ml four neck round bottom flask, which is equipped with a stirrer, a thermometer and a condenser, 750 grams small particle size encapsulated viscosity reducing additive latex obtained in the above described procedure are heated to 90°C. The agglomerating agents are concentrated ammonia (29.3% by weight) and acetic acid (50% by weight) used as two separate solutions. To the 90°C stirred emulsion, ammonia and acetic acid solutions are added alternately in 0.30 ml and 0.54 ml increment every 5 minutes. The latex particle size is measured after each addition. The agglomeration process is stopped when the desired particle size is achieved (usually 200 - 250 nm). The agglomerated latex is mixed with 8.03 grams 28% sodium lauryl sulfate solution and then cooled to 53°C.

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Encapsulation by Methyl Methacrylate

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Under nitrogen sweep, 1.79 grams 28% sodium lauryl sulfate solution, 25 grams of methyl methacrylate and 0.1 grams of n-dodecyl mercaptan are added to the above agglomerated emulsion. Water (54 grams) is used to rinse the containers for the added materials. After the mixture is stirred for 10 minutes, 0.0375 grams sodium sulfoxylate formaldehyde dissolved in 10 grams water and 0.0375 grams sodium persulfate dissolved

in 10 grams water are added to the reaction mixture. After an exotherm is observed, the residual monomer is further reacted by addition of 0.012 grams sodium sulfoxylate formaldehyde which is dissolved in 4 grams of water and 0.012 grams sodium persulfate which is dissolved in 4 grams of water. The final emulsion is held at 55°C for 1 hour and then cooled to room temperature.

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Coagulation of the Microagglomerated Encapsulated Viscosity Reducing Additive

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In a 4000 ml beaker, 1667 grams 0.475 % calcium chloride solution is heated to 70°C. Under agitation, 833 grams of the above encapsulated emulsion is slowly poured into the calcium chloride solution. The mixture is allowed to be stirred for 15 minutes and then filtered to remove water. The wet coagulum is washed with 1250 grams water and filtered to remove water. The coagulated polymer is dried in a fluid bed dryer at 80°C. This is Polymer D.

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Example 5 Co-microagglomerated Acrylic Impact modifier and Encapsulated Viscosity Reducing Additive

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Small Particle Size Acrylic Impact Modifier

Same as the small particle size acrylic impact modifier in example 1 (Latex A-1).

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Small Particle Size Encapsulated Viscosity Reducing Additive

Same as the small particle size encapsulated viscosity reducing additive in Example 4 (Latex D-1).

Co-microagglomeration

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In a 1000 ml four neck round bottom flask, which is equipped with a stirrer, a thermometer and a condenser, 375 grams small particle size impact modifier latex obtained by the procedure described in Example 1 and 375 grams small particle size encapsulated viscosity reducing additive latex D-1 prepared by the procedure in Example 4 are heated to 90°C. The agglomerating agents are concentrated ammonia (29.3% by weight) and acetic acid (50% by weight) used as two separate solutions. To the 90°C stirred emulsion, ammonia and acetic acid solutions are added alternately in 0.30 ml and 0.54 ml increment every 5 minutes. The latex particle size is measured after each addition. The agglomeration process is stopped when the desired particle size (25 nm) is achieved. The agglomerated latex is mixed with 8.92 grams 28% sodium lauryl sulfate solution then cooled to 53°C.

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Encapsulation by Methyl Methacrylate

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Under nitrogen sweep, 1.78 grams 28% sodium lauryl sulfate solution, 25 grams of methyl methacrylate and 0.1 grams of n- dodecyl mercaptan are added to the above agglomerated emulsion. 69 grams water is used to rinse the containers for the added materials. After the mixture is stirred for 10 minutes, 0.0375 grams sodium sulfoxylate formaldehyde dissolved in 10 grams water and 0.0375 grams sodium persulfate dissolved in 10 grams water are added to the reaction mixture. After an exotherm is observed, the residual monomer is further reacted by addition of 0.013 grams sodium sulfoxylate formaldehyde which is dissolved in 4 grams of water and 0.013 grams sodium persulfate which is dissolved in 4 grams of water. The final emulsion is held at 55°C for 1 hour and then cooled to room temperature.

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Coagulation of the co-microagglomerated Acrylic Impact Modifier and Viscosity Reducing Additive

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In a 4000 ml beaker, 1667 grams 0.475 % calcium chloride solution is heated to 70°C. Under agitation, 833 grams of the above encapsulated emulsion is slowly poured into the calcium chloride solution. The mixture is allowed to be stirred for 15 minutes and then filtered to remove water. The wet coagulum is washed with 1250 grams water and filtered to remove water. The coagulated polymer is dried in a fluid bed dryer at 80°C. This is Polymer E

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Testing Results:1) PVC Fusion.

5 The test is made on a Haake System 90 torque rheometer. The mixing chamber is heated to 170°C. The rotating speed of the mixing paddles is set at 50 rpm. The microagglomerated additives are mixed with a pre-blended poly(vinyl chloride) master batch according to the following formulations. The mixed powder is then charged into the heated mixing chamber. The torque and temperature changes are recorded. The speed of gelation or fusion is characterized by the Time to Peak Torque and the Temperature of the mixture at the time 10 (Peak Temperature). Excessively long fusion times are less desirable.

15	Poly(vinyl chloride) Master Batch			K58 PVC	100
				Organotin Stabilizer	2.0
				Glycerol monostearate	0.5
				Oxidized polyethylene wax	0.2
				Microagglomerated additive (s)	0, 7 or 14
20	A Impact modifier only	B Viscosity reducing additive only	C Coaggl. and encaps. A-1//B-1//shell 45//45//10	Time To Peak Torque (seconds)	Peak Temperature (°C)
25	0	0	0	47	163
	0	7	0	264	178
	7	7	0	218	176
30	0	0	14	161	175
35	A Impact modifier only	D Viscosity reducing additive only	E Coaggl. and encaps. A-1//D-1//shell 45//45//10	Time To Peak Torque (seconds)	Peak Temperature (°C)
40	0	0	0	47	163
	0	10	0	259	178
	10	10	0	188	176
	0	0	20	165	176

Example: Powder Compaction Properties

45 A major advantage to coagglomerating the small particle size acrylic impact modifiers and flow improving processing aids is that it facilitates isolation of the flow improving additives, which tend to compact. The data from a Hosokawa powder compaction test illustrate this advantage. The testing was done on 52 ml of powder placed in a stainless steel cup, covered and loaded on top with a lead weight of 964.2 g. The cup and weight were placed in an automatic tapping device and tapped for 180 seconds. The cover and weight were then removed from the cup and the cup contents were carefully pressed out using the false bottom of the cup onto a screen with 2 mm openings (No. 10 screen). The screen was then vibrated for 60 seconds using a rheostat dial setting of 4.5. The weight of any polymer remaining on the screen following the 60 seconds of vibration was recorded. The weight of remaining polymer was divided by the total weight of polymer used to obtain the fraction of polymer remaining on the screen, which is reported in the table below. Two measurements were done for each sample. It is seen the co-microagglomerated materials pass more completely through the screen.

		Fraction of Polymer Remaining On Screen			
		Sample	Run 1	Run 2	Average
5		B: Microagglomerated Viscosity Reducing Additive	0.987	0.981	0.984
10		C: Co-microagglomerated Acrylic Impact Modifier and Viscosity Reducing Additive	0.327	0.323	0.325
15		D: Microagglomerated Multistage Flow Improving Additive	0.624	0.690	0.657
20		E: Co-microagglomerated Acrylic Impact Modifier and Multistage Flow Improving Additive	0.246	0.333	0.289

Example: Impact Measurements on PVC Milled /Moulded Plaques

Co-microagglomeration of the acrylic impact modifiers and flow improving additives does not reduce the effectiveness of the impact modification provided to the PVC by the additives compared with a simple physical blend of the additives. This is illustrated by the notched Izod impact measurements made on milled and moulded PVC plaques described in this example.

Blending of PVC Formulation

A PVC masterbatch was prepared by blending the PVC resin, heat stabilizer, and lubricants specified in the table below in a 5-lb high intensity mixer. The blending procedure involved mixing the PVC resin alone in the high-intensity mixer until it shear heated to 52°C. The liquid organo-tin stabilizer was then added to the blend. The blend was allowed to shear heat to 66°C and the lubricants were added to the blend. High intensity mixing was continued with the addition of steam to the mixer jacket until the blend temperature reached 95°C. The blend was then cooled with only slow stirring to 60°C by circulating water through the mixer jacket. The blend, which will be referred to as the PVC masterbatch, was removed from the mixer at approximately 60°C. The individual blends containing the microagglomerated additives were prepared by hand mixing the amounts of PVC masterbatch and microagglomerated additives specified in the table below.

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PVC Mill/Moulding Masterbatch Formulation

5 100.0 phr PVC (K=60) Resin
 2.0 phr dimethyltin bis(2-ethylhexylthioglycolate)
 2.7 phr glycerol monostearate
 0.3 phr polyolefin wax - external lubricant
 1.0 phr high Mw poly(MMA/EA) copolymer
 10 8.0 phr core/shell BA//MMA copolymer
 1.5 phr TiO₂
 0, 4 or 8 phr Flow Improving Additive

	<u>Blend</u>	<u>PVC Masterbatch</u>	<u>Microagglomerated Additives</u>
15	1	105.0 phr	None
	2	105.0 phr	7 phr A: Small particle size acrylic impact modifier + 7 phr B: Microagglomerated flow improving additive
20	3	105.0 phr	14 phr C: Co-microagglomerated acrylic impact modifier and flow improving additive
	4	105.0 phr	10 phr A: Small particle size acrylic impact modifier + 10 phr D: Microagglomerated multistage flow improving additive
25	5	105.0 phr	20 phr E: Co-microagglomerated acrylic impact modifier and multistage flow improving additive

Milling and Moulding PVC Plaques

30 The PVC powder blends were milled on a two-roll mill heated to 177°C for five minutes. The fused sheet was removed from the mill and pressed in a metal picture frame mould to form a 14 cm x 24.1 cm x 0.32 cm plaque. The moulding was done in a 177°C press by heating the mould for three minutes under light pressure, applying a 70 ton pressure for two minutes, and then transferring the mould to a cold press to cool for five minutes

Notched Izod Impact Measurements

40 Izod bars were cut from the moulded plaques and notched in accordance with ASTM Standard D256. The samples were tested at 23°C and 18°C. Impact measurements were made on five bars for each blend. The results for Izod bars cut with their long direction in the machine direction of the plaques are shown in the tables below.

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Notched Izod Impact Measurements at 23°C

5	Blend	Notched Izod Impact Strength (J/m)			
		Hinge Breaks	Clean Breaks	Impact Strength	Number of Samples
10	1: PVC Masterbatch	--	0	32 J/m	5
15	2: PVC Masterbatch + 7 phr A + 7 phr B	544 J/m	3	11	2
20	3: PVC Masterbatch + 14 phr C	523	4	11	1
25	4: PVC Masterbatch + 10 phr A + 10 phr D	918	41	1	
	5: PVC Masterbatch + 20 phr E	902	5	--	0

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Notched Izod Impact Measurements at 18°C

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Notched Izod Impact Strength (J/m)

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Blend	Hinge Breaks		Clean Breaks	
	Impact Strength	Number of Samples	Impact Strength	Number of Samples
1: PVC Masterbatch	---	0	32 J/m	5
2: PVC Masterbatch + 7 phr A + 7 phr B	---	0	75	5
3: PVC Masterbatch + 14 phr C	---	0	75	5
4: PVC Masterbatch + 10 phr A + 10 phr D	897 J/m	5	---	0
5: PVC Masterbatch + 20 phr E	865	5	---	0

Example: Spiral Flow Measurements

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Co-microagglomeration of the acrylic impact modifiers and flow improving additives does not reduce the flow improvement of the PVC resulting from the additives when compared with a formulation containing a simple physical blend of the additives. This is shown in spiral flow measurements on PVC injection moulding formulations made using a spiral mould in an injection moulding machine as described below.

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Blending

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The PVC injection moulding formulations were prepared by blending the PVC resin, the heat stabilizer, and the lubricants specified below in a 35-lb Henschel mixer. The blending procedure involved mixing the PVC resin alone in the high-intensity mixer until it shear heated to 52°C. The liquid organo-tin stabilizer was then added to the blend. The blend was allowed to shear heat to 66°C and the lubricants were added to the blend. High intensity mixing was continued until the blend temperature reached 95°C. The blend was then cooled with only slow stirring to 60°C by circulating water through the mixer jacket. The blend, which will be referred to as the PVC masterbatch, was removed from the mixer at approximately 60°C.

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The blends containing the impact modifiers and processing aids were prepared by mixing the desired amounts of PVC masterbatch and the additives together in a 5-lb high intensity blender at room temperature for five minutes (the blend temperature will exceed room temperature due to shear heating but no additional heat was applied).

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PVC Injection Moulding Masterbatch Formulation

5 100.0 phr PVC (K=60) Resin
 2.0 phr dimethyltin bis(2-ethylhexylthioglycolate)
 2.7 phr glycerol monostearate
 0.3 phr polyolefin wax - external lubricant
 1.0 phr high Mw poly(MMA/EA) copolymer
 10 8.0 phr core/shell BA//MMA copolymer
 1.5 phr TiO₂
 0, 4 or 8 phr Flow Improving Additive

15	<u>Blend</u>	<u>PVC Masterbatch</u>	<u>Impact Modifiers and Processing Aids</u>
	1	105.0 phr	1.0 phr HMW-PA
20	2	105.0 phr	1.0 phr HMW-PA + 8.0 phr A: Small particle size acrylic impact modifier + 8.0 phr B: Microagglomerated flow improving additive
25	3	105.0 phr	1.0 phr HMW-PA + 16.0 phr C: Co-microagglomerated acrylic impact modifier and flow improving additive

Extruding and Pelletizing

30 The blends were extruded using an American Leistritz counter-rotating twin-screw extruder and pelletized. The extruder is equipped with 34 mm counter-rotating screws. There are five barrel sections giving a total length to diameter ratio of 15.9. The barrel temperatures were set at 140°/145°/150°/155°C (Note: no heat to first barrel) and the die temperature was set at 160°C. The blends were extruded into a single strand through a 3.2 mm diameter die and cooled by passing through a water bath before being chopped into pellets.

Injection Moulding

40 The spiral flow moulding was done using a spiral shape Master Unit Die insert in an Arburg 270-90-350 injection moulding machine. The injection moulding machine had a 22 mm diameter screw with a length to diameter ratio of 20.5 and a compression ratio of 2.1. The barrel temperatures were set at 146°, 171°, and 177°C and the nozzle temperature was set at 186°C. The screw speed was set at 200 rpm. These settings produced a melt temperature of approximately 210°C as measured for an air shot using a hand-held pyrometer with a needle probe. The mould temperature was 32°C. Spirals were injection moulded for three different injection pressures: 495 bar, 720 bar, and 1590 bar.

Spiral Flow Measurements

45 The spiral flow lengths obtained for the three different injection pressures are shown in the table below for Blends 1, 2, and 3. The values in the table represent the averages and the standard deviations (in parentheses) for five spiral length measurements. The measurements indicate that the flow of the PVC masterbatch (Blend 1) is improved when the flow improving additive is present and that the flow of the PVC blend in which the impact modifier is co-microagglomerated with the flow improving additive (Blend 3) is equivalent to the blend in which the microagglomerated impact modifier and the microagglomerated flow improving additive are blended separately (Blend 2).

Spiral Flow Measurements				
5	Blend	Spiral Flow Length (cm) for Injection Pressure P		
		P=495 bar	P=720 bar	P=1590 bar
10	1	9.4 (± 0.6)	18.7 (± 0.1)	51.9 (± 0.2)
	2	11.5 (± 0.1)	20.5 (± 0.4)	52.5 (± 0.2)
	3	12.2 (± 0.1)	21.1 (± 0.0)	52.9 (± 0.4)

Claims

15 1. A blend of core/shell impact modifier polymer and core/shell processing aid polymer wherein:

(a) the impact modifier polymer comprises particles of:

(1) rubbery first core polymer particle having a glass temperature below -20°C and an average particle size below 100 nm diameter, and containing at least 50 weight percent of units derived from butadiene, (C₂ to C₈)alkyl esters of acrylic acid, or mixtures thereof, and having a weight-average molecular weight of at least 500,000; and

(2) first intermediate shell polymer having a glass temperature above -20°C, and containing more than 50 weight percent units derived from (C₁ to C₄)alkyl esters of acrylic or methacrylic acid and being from 5% to 20% by weight of the core/intermediate shell impact modifier polymer particles;

20 (b) the processing aid polymer component comprises particles of:

(1) second core polymer particle having a particle size below 100 nm diameter and containing from at least 80 weight percent of units derived from (C₄ to C₁₂)alkyl esters of acrylic acid or methacrylic acid or mixtures thereof and from 0 to 20 parts of units derived from at least one other vinyl or vinylidene monomer, and having a weight-average molecular weight of no more than 100,000 and being free from units derived from graftlinking or crosslinking monomer and not being deliberately crosslinked; and at least one of:

(2) a second intermediate crosslinked shell polymer containing

a) at least 90 weight percent of units derived from one or more vinyl aromatic monomer and/or (C₁ - C₄)alkyl esters of (meth)acrylic acid,

b) from 0.5 to 10 weight percent of units derived from at least one of:

(i) multifunctional monomer containing two or more copolymerizable double bonds; or

(ii) alkali, alkaline earth, or transition metal salt of a copolymerizable unsaturated acid; or

25 (3) a third intermediate shell polymer containing at least 70 weight percent of units derived from one or more vinyl aromatic monomer or (C₁ to C₄)alkyl esters of methacrylic acid; and

30 (c) an encapsulating shell of hard polymer having a glass temperature of at least 60°C and containing more than 50% by weight of (C₁ to C₄)alkyl ester of methacrylic acid and being present in an amount of from 5 to 20% by weight of the final core/shell polymer blend and encapsulating an aggregation of impact modifier and processing aid particles and forming a particle of at least 150 nm diameter.

35 2. A blend of Claim 1 wherein at least one of the encapsulating shell (c), the first intermediate shell polymer (a.2), or the third intermediate shell stage (b.3) comprises more than 50% methyl methacrylate units.

40 3. A blend of Claim 1 or 2 wherein the rubbery first core polymer particle (a.1) contains more than 50% n-butyl acrylate units and/or contains units derived from at least one multiunsaturated monomer, preferably allyl methacrylate, allyl acrylate, diallyl maleate, diallyl fumarate, divinylbenzene, a di- or triacrylate ester of a polyol, and/or a di- or trimethacrylate ester of a polyol.

45 4. A blend of any preceding claim wherein the (C₄ to C₁₂)alkyl ester of acrylic acid or methacrylic acid in the second core polymer particle (b.1) is butyl acrylate.

50 5. A blend of any preceding claim wherein the salt of the copolymerizable unsaturated acid in the second intermediate crosslinked polymer shell (b.2) comprises at least one salt of methacrylic acid, acrylic acid, itaconic acid, maleic acid, fumaric acid, alpha-methylene-delta-methyladipic acid, or acryloxypropionic

acid, preferably the sodium salt thereof.

6. A toughened blend which comprises:
 - (a) from 5 to 40 parts of blend of any preceding claim;
 - (b) from 60 to 95 parts of thermoplastic matrix resin, preferably homopolymer or copolymer of vinyl chloride;
 - optionally in the form of moulded, extruded or other shaped article.
7. A blend of Claim 6 wherein the final core/shell polymer blend is dispersed into domains of particle size substantially equivalent to those of the particles of the non-aggregated core /intermediate shell polymers.
8. A process for preparing a blend of core/shell impact modifier polymer and core/shell processing aid polymer which comprises:
 - (a) forming by emulsion polymerization a rubbery first core particulate polymer, having a glass temperature below -20°C and an average particle size below 100 nm diameter, from a monomer mixture containing at least 50 weight percent butadiene, (C₂ to C₈)alkyl esters of acrylic acid, or a mixture thereof, to a weight-average molecular weight of at least 500,000;
 - (b) in the presence of the polymer product of (a) and under conditions wherein substantially no new polymer particles are formed, forming by sequential emulsion polymerization first intermediate shell polymer, having a glass temperature above -20°C and comprising more than 50% by weight units of (C₁ to C₄)alkyl ester of acrylic or methacrylic acid, and in an amount of first intermediate shell from 5% to 20% by weight of the first core/intermediate shell polymer particles (8.a) plus (8.b);
 - (c) separately forming, by emulsion polymerization, particulate second core polymer, having a particle size below 100 nm diameter, and comprising at least 80 weight percent of (C₄ to C₁₂)alkyl esters of acrylic acid or methacrylic acid or mixtures thereof, from 0 to 20 percent of units of at least one other vinyl or vinylidene monomer but free from graftlinking or crosslinking monomer units, to a weight-average molecular weight of no more than 100,000, without deliberately crosslinking the polymer;
 - (d) optionally, forming by sequential emulsion polymerization in the presence of the second core polymer (c), under conditions wherein substantially no new polymer particles are formed, second intermediate crosslinked shell polymer containing:
 - (1) at least 90 weight percent of units of one or more vinyl aromatic monomer and/or (C₁ to C₄)alkyl esters of (meth)acrylic acid;
 - (2) from 0.5 to 10 weight percent of units of at least one of:
 - a) multifunctional monomer containing two or more copolymerizable double bonds;
 - b) copolymerizable unsaturated acid, which units are partially to completely in the form of an alkali, alkaline earth, or transition metal salt;
 - (e) optionally, forming by sequential emulsion polymerization in the presence of the second core polymer or the second core/ intermediate crosslinked shell polymer and under conditions wherein substantially no new polymer particles are formed, third intermediate shell stage of polymer containing at least 70 weight percent of units of one or more vinyl aromatic monomers or (C₁ to C₄)alkyl esters of methacrylic acid;
 - wherein at least one of steps (d) or (e) must be conducted;
 - (f) admixing the polymer particles formed in steps (a-b) and in steps (c-e) in emulsion form;
 - (g) aggregating the core/intermediate shell polymer particles to form a dispersion of aggregated particles of at least 150 nm diameter;
 - (h) forming, by sequential emulsion polymerization onto the aggregated particles, under conditions wherein substantially no new polymer particles are formed, an encapsulating shell of hard polymer having a glass temperature of at least 60°C and comprising more than 50% by weight units of (C₁ to C₄)alkyl ester of methacrylic acid, in an amount of encapsulating shell from 5 to 20% by weight of the final core/shell polymer blend; and
 - (i) isolating the final core/shell polymer blend.
9. A process of Claim 8 wherein the final core/shell polymer blend is isolated by spray-drying or coagulation, preferably by addition of an aqueous solution of salt of inorganic acid.
- 55 10. A process of Claim 8 or 9 wherein a stabilizer is incorporated into the emulsion of the final core/shell polymer blend prior to isolation and wherein the stabilizer contains antioxidant and/or thermal stabilizer.
11. A process of claim 8, 9 or 10 wherein aggregation of the core/intermediate shell polymer particles is ac-

complished by addition of separate streams of
(a) aqueous solution of weak base, preferably ammonium hydroxide; and
(b) aqueous solution of weak acid, preferably acetic acid.

5 12. A process of claim 8, 9 or 10 as applied to the preparation of polymer blend of any of claims 2 to 7.

13. A process for preparing a toughened thermoplastic resin which comprises:
(a) forming a final core/shell polymer blend by the process of any of claims 8 to 12; and
10 (b) blending the final core/shell polymer with a thermoplastic matrix resin under conditions of heat and shear sufficient to cause the final core/shell polymer to disperse into domains of particle size equivalent to those of the particles of the core/intermediate shell polymers prior to aggregation.

14. A process of claim 13 wherein the toughened thermoplastic resin is further processed into a toughened article by extrusion or by injection moulding.

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European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 8893

DOCUMENTS CONSIDERED TO BE RELEVANT						
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)			
A	WO-A-8 805 450 (THE DOW CHEMICAL COMPANY) * claims 1-6 * * examples * * page 3, line 4 - line 26 * ---	1	C08F285/00 C08L27/06 //(C08F285/00, 220:12)			
A	EP-A-0 354 330 (MITSUBISHI RAYON CO. LTD) * claims * ---	1				
A	EP-A-0 404 972 (MITSUBISHI RAYON CO. LTD) * claims * * examples * -----	1				
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)			
			C08F C08L			
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search THE HAGUE</td> <td>Date of completion of the search 30 NOVEMBER 1992</td> <td>Examiner PERSSON</td> </tr> </table>				Place of search THE HAGUE	Date of completion of the search 30 NOVEMBER 1992	Examiner PERSSON
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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document				

